

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE  
 in its capacity as elected Office

Date of mailing (day/month/year) 08 June 2001 (08.06.01)	
International application No. PCT/EP00/09590	Applicant's or agent's file reference C3957(C)/rkk
International filing date (day/month/year) 27 September 2000 (27.09.00)	Priority date (day/month/year) 01 October 1999 (01.10.99)
Applicant JARVIS, Anthony, Nicholas et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
 29 March 2001 (29.03.01)

☐ in a notice effecting later election filed with the International Bureau on:  
 \_\_\_\_\_

2. The election ☒ was

☐ was not

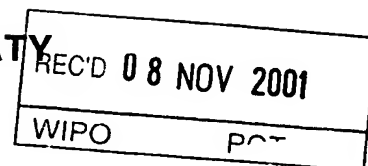
made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Olivia TEFY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38



# PATENT COOPERATION TREATY

## PCT



### INTERNATIONAL PRELIMINARY EXAMINATION REPORT



(PCT Article 36 and Rule 70)

Applicant's or agent's file reference C3957(C)/rkk	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/09590	International filing date (day/month/year) 27/09/2000	Priority date (day/month/year) 01/10/1999
International Patent Classification (IPC) or national classification and IPC C11D3/37		
Applicant UNILEVER PLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  29/03/2001	Date of completion of this report  06.11.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Culmann, J-C  Telephone No. +49 89 2399 8487  



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/09590

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, pages:

1,2,4,6-8,10-18 as originally filed

3,5,9 as received on 13/10/2001 with letter of 10/10/2001

### Claims, No.:

3 (part),4-11 as originally filed

1,2,3 (part) as received on 13/10/2001 with letter of 10/10/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/09590

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations  
**see separate sheet**





*HarCor#2*

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability**

***Novelty (Article 33(2) PCT)***

The subject-matter of claims 1 to 11 is novel, but does not involve an inventive step in the sense of Article 33(3) PCT.

***Inventive step (Article 33(3) PCT)***

1. The problem faced by the Applicants is manifold:

- conferring increased dimensional stability to the treated fabric;
- improving the surface colour definition;
- as well as the ease in the handling of the fabrics;
- in both industrial textile treatment processes, in small and large scale laundering processes.

Last but not least, a good conditioning was also aimed at.

2. D1 (GB-A-2 005 322) is the closest state of the art, because

- it relates to textile treatment compositions;
- which compositions comprise an anionic polymer of the formula found in current claim 3 of the application;
- which compositions confer not only shrink resistance, but also (as is clear from the experimental part) prevent dye transfers.

These textile treatment compositions also comprise an exhaustion agent, see D1



on page 2 lines 22 to 26, which may be any soluble compound, particularly alkali metal, alkaline earth or ammonium salts of strong acids.

3. The Applicants investigated the change of coloured regions of a cotton fabric after treatment with a composition according to current claim 1 and after treatment with a neat fabric softening composition, as well as a composition comprising the anionic polymer according to item a) of current claim 1.

From the experimental data, it remains however that it may not be determined whether any observed improvement as to the colour is due

- i) to the exhaustion of the anionic polymer; or is due
- ii) to the very nature of the exhausting material.

The former explanation means that the observed effect is not related to the nature of the exhaustion material: the consequence would be that the effect would be merely related to the quantity of anionic polymer deposited onto the fabric.

Since the same anionic polymer is also exhausted onto fabrics according to the process of D1, the investigations of the Applicants would amount to nothing else as providing some technical information as to a compulsorily achieved (when exhaustion is complete) phenomenon (reduced change of colour) unrelated to the fabric conditioning nature of the cationic agent of item b) of current claim 1.

In this event, the objective problem achieved by the subject-matter of claim 1 over D1 would be the selection, within the group of the exhaustion agents, of those presenting further advantages in the field of the fabric care compositions.

The man skilled in the art knows furthermore that:

- quaternary ammonium salts having lipophilic substituents are fabric softening materials;
- they are also soluble to some extent in water.



Since D1 generally suggests ammonium salts (among others, see on page 2, lines 22 to 27) as exhaustion agents, does not set specific restrictions, the man skilled in the art would thus select quaternary ammonium fabric conditioning agents in order to have an exhaustion agent which provides a further, expectable fabric conditioning effect.

And the whole of the present application would thus lack an inventive step pursuant to Article 33(3) PCT.

There is nothing in the whole application in favour of the second hypothesis, i.e., the fabric conditioning nature of the cationic agent has an impact on the effect (no difference is established over other cations; or for specific fabric conditioning agents over others); for the purpose of this report, and in the state of the file, said second hypothesis has to be ignored. Incidentally, the exhausting effect is not a "salting effect", since D1 specifies (see on page 2, line 27) that divalent cations are twice as effective as monovalent ones.

*Nota bene:* considering the objective problem as stated above, the man skilled in the art could have also considered the mere addition of a fabric conditioning quaternary ammonium salt, to a composition comprising the anionic polymer and a less expensive exhaustion agent; he would have still arrived at something falling within the scope of claim 1. A plurality of obvious solutions does not make any one of them not obvious for the man skilled in the art.

### ***Further comments***

As to the arguments put forward by the Applicants, it may be noted that nonionic conditioners cannot be exhaustion agents because they are not charged.

Since all quaternary ammonium salt softeners are charged, they are exhaustion agents.

The Examining Authority has appreciated the willingness of the Applicants to deal with the objections and the matters raised; as the fairness of their



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP00/09590

comments/reply.



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# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>C3957(C)/rkk</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 00/09590</b>	International filing date (day/month/year) <b>27/09/2000</b>	(Earliest) Priority Date (day/month/year) <b>01/10/1999</b>
Applicant  <b>UNILEVER PLC et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

### 4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

### 5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

### 6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/09590

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D C08G D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 335 404 A (LION CORP) 4 October 1989 (1989-10-04) abstract	1,5-11
A	GB 2 005 322 A (IWS NOMINEE CO LTD) 19 April 1979 (1979-04-19) cited in the application claims 1,3,4,9,10	1-4,9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

16 January 2001

Date of mailing of the international search report

23/01/2001

Name and mailing address of the ISA

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Authorized officer

Saunders, T



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/09590

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0335404 A	04-10-1989	JP 1250473 A	05-10-1989
		JP 1580169 C	11-10-1990
		JP 2004709 B	30-01-1990
GB 2005322 A	19-04-1979	AU 520469 B	04-02-1982
		AU 3868078 A	07-02-1980
		DK 344878 A,B,	05-02-1979
		ES 472340 A	16-11-1979
		FI 782389 A,B,	05-02-1979
		GR 64927 A	09-06-1980
		IT 1098008 B	31-08-1985
		NZ 188034 A	26-08-1980
		PT 68354 A	01-08-1978
		US 4225312 A	30-09-1980
		ZA 7804438 A	25-07-1979



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Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

**0 335 404  
A2**

12

## EUROPEAN PATENT APPLICATION

21 Application number: 89105663.2

51 Int. Cl.4: **C11D 1/835 , C11D 3/37**

22 Date of filing: 30.03.89

30 Priority: 31.03.88 JP 79228/88

43 Date of publication of application:  
04.10.89 Bulletin 89/40

84 Designated Contracting States:  
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54 **Liquid softener composition.**

57 A liquid softener composition comprising:

(A) a slightly water-soluble quaternary ammonium salt type cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;

(B) a carboxylic acid type anionic polymer;

(C) a polyoxyethylene adducted nonionic surfactant; and

(D) an aqueous vehicle,

wherein the weight ratio of (A)/(C) is within range of from 100/1 to 3/1.

**EP 0 335 404 A2**

## LIQUID SOFTENER COMPOSITION

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

The present invention relates to a softener composition which can impart, for example, an excellent softness and antistatic property to fiber, clothing, and hair. More specifically, it relates to an aqueous liquid softener composition which can impart an excellent softness and antistatic property to chemical textile products such as of acryl, nylon, polyester, and also has an excellent dispersion stability.

## 2. Description of the Related Art

Heretofore, to prevent deterioration of the touch and antistatic properties of textile products after repeated wear and washing, a softener containing a quaternary ammonium salt having two long chain alkyl groups or alkenyl groups in the molecule as the main component has been employed. Representative examples of the quaternary ammonium salts include di-hardened tallow alkyldimethylammonium chloride, and methyl-1-tallow amidoethyl-2-alkylimidazolium methylsulfate, but these single products, although they are capable of imparting excellent softness to cotton products, have no sufficient effect from the view point of imparting softness and an antistatic property to chemical fiber products. Accordingly, proposals have been made to modify the quaternary ammonium salt itself (Japanese Unexamined Patent Publication (Kokai) No. 55-51876); use of the quaternary ammonium salt in combination with another specific di-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) Nos. 55-51874, 55-62268, 55-103364, 55-103365); use of the quaternary ammonium salt in combination with a tri-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) Nos. 55-112375, 55-112377, 56-79768); use of the quaternary ammonium salt in combination with a specific mono-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) No. 57-205581); or, use of the quaternary ammonium salt in combination with an anionic surfactant (Japanese Unexamined Patent Publication (Kokai) Nos. 53-19497, 53-38794, 53-52799, 58-13775). Nevertheless, although some improvement can be observed when these compositions are used, the effects are still unsatisfactory, or on the contrary, the softness of cotton may be worsened in some cases. Thus, up to data, a softener for domestic use which can impart a sufficient softness to both textile products of cotton and chemical fibers, and provide an excellent antistatic effect for chemical fibers, is not available.

On the other hand, the present Applicant has found that an excellent effect can be obtained by use of a carboxylic acid type anionic polymer in combination with a quaternary ammonium salt and has filed a patent application therefor (Japanese Patent Application No. 62-127722). Nevertheless, when only these two components are used, it has been found that a phase separation after a lapse of days for storage or abrupt rise in viscosity elevation occurs, whereby no sufficient dispersion stability which is essential to the commercial product cannot be satisfactorily obtained. Separately from these, proposals have been made for granular additives to a detergent by using a dilong chain alkyl quaternary ammonium salt in combination with a specific anionic polymer (Japanese Unexamined Patent Publication (Kokai) Nos. 59-6298, 61-7398), but such granular products can not be sufficiently dispersed or dissolved in water, and therefore, the object of the present invention cannot be accomplished even by using such a granular additive for the conventional washing and rinsing steps.

## SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to obviate the above-mentioned problems in the prior art and to provide an aqueous liquid softener composition which can impart the same softness to cotton as that of the prior art products, but a much greater softness and antistatic property to chemical fibers, compared with the prior art products in softening treatment practiced in the washing and rinsing steps at home, and further, has an excellent dispersion stability.



Other objects and advantages of the present invention will be apparent from the description set forth hereinbelow.

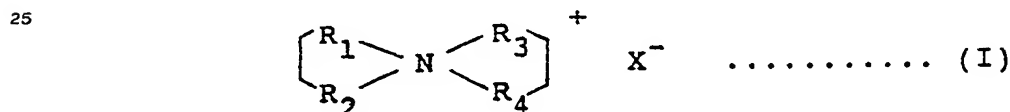
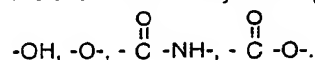
In accordance with the present invention, there is provided a liquid softener composition, comprising:

- (A) a slightly water-soluble quaternary ammonium salt type cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;  
 (B) a carboxylic acid type anionic polymer;  
 (C) a polyoxyethylene adducted nonionic surfactant; and  
 (D) an aqueous vehicle, with the weight ratio of (A)/(C) being within range of from 100/1 to 3/1.

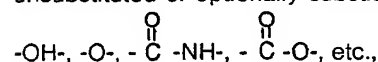
# DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been found that the above-mentioned object of the present invention can be accomplished by using a specific slightly water-soluble quaternary ammonium salt type cationic surfactant in combination with a carboxylic acid type anionic polymer and a polyoxyethylene adducted nonionic surfactant.

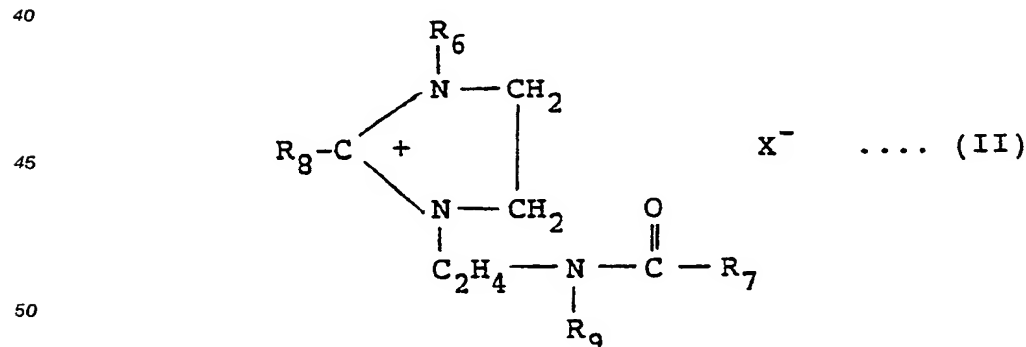
The slightly water-soluble quaternary ammonium salt of the component (A) usable in the present invention may be exemplified by those represented by the formula (I) or (II) shown below. These compounds can be used alone or as a mixture of two or more compounds, and these are cationic surfactants having 2 or 3 straight or branched alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule which may be respectively optionally substituted or intermingled with functional groups such as



wherein at least two groups of  $\text{R}_1 - \text{R}_4$  represent straight or branched alkyl or alkenyl groups which may be unsubstituted or optionally substituted by



the remainder of the groups of  $\text{R}_1 - \text{R}_4$  represent an alkyl group with 1 to 3 carbon atoms, a hydroxyalkyl group or a group represented by the formula  $-(\text{C}_2\text{H}_4)_l\text{H}$  (where  $l$  is an integer of 1 to 5, and  $\text{X}$  represents a halogen or a monoalkylsulfate group represented by  $\text{R}_5\text{SO}_4$  where  $\text{R}_5$  represents an alkyl group with 1 to 3 carbon atoms).



wherein  $\text{R}_6$  represents an alkyl group with 1 to 4, preferably 1 to 2 carbon atoms,  $\text{R}_7$  and  $\text{R}_8$  each represent an alkyl or alkenyl group with 14 to 24 carbon atoms,  $\text{R}_9$  represents hydrogen or an alkyl group with 1 to 4 carbon atoms, and  $\text{X}$  has the same meaning as in the formula (I).

At least two groups of  $\text{R}_1 - \text{R}_4$  in the above formula (I) have 14 to 24, preferably 16 to 22 carbon atoms,  $\text{R}_7$  and  $\text{R}_8$  in the above formula (II) have 14 to 24, preferably 15 to 21 carbon atoms, each group may have

a distribution within these ranges, and the respective groups may be either the same or different from each other. When the carbon number is lower than this range, for example, when a mixture of quaternary ammonium salts of (I) or (II) synthesized from coconut fatty acids is used, the softness will be poor.

Specific examples of the component (A) include one or a mixture of two or more of di-hardened tallow alkyldimethylammonium chloride, di-tallow alkyldimethylammonium bromide, dioleyldimethylammonium chloride, dipalmitylhydroxyethylammonium methylsulfate, distearylmethylpolyoxyethylene (average degree of polymerization is 3) ammonium chloride, diisostearyldimethylammonium methylsulfate, dieicosyldimethylammonium chloride, dibehenylmethylpolyoxyethylene (average degree of polymerization is 5) ammonium chloride, dierucyldimethylammonium chloride, di[2-dodecanoylamino]ethyl]-dimethylammonium chloride, di[2-stearoylamino]propyl]-dimethylammonium ethylsulfate, di(2-ethylpalmitoyl)-hydroxyethylmethylammonium methylsulfate, trioleylmethylammonium chloride, dioleymonostearyl-methylammonium chloride, dioleymonobehenylmethylammonium chloride, monooleyldierucylmethylammonium chloride, tristearylmethylammonium methylsulfate, methyl-1-tallow amidoethyl-2-tallow alkylimidazolium methylsulfate, methyl-1-hexadecanoylamidoethyl-2-pentadecylimidazolium chloride, ethyl-1-octadecenoylamidoethyl-2-heptadecenylimidazolium ethylsulfate, and the like. The content of the component (A) in the softener composition may be as desired but is preferably 3 to 50% by weight (hereinafter abbreviated merely as %), more preferably 4 to 20%.

As the carboxylic acid type anionic polymer of the component (B), homopolymers of ethylenically unsaturated carboxylic acids or anhydrides thereof or copolymers of said monomers can be used. The salts of these homopolymers and copolymers may be used. Also, these polymers may be used either as such or in the form of water soluble neutral salts such as alkali metal salts or alkaline earth metal salts. The component (B) has an average molecular weight generally of 500 to 50,000, preferably 500 to 20,000, and more preferably 500 to 10,000.

The above-mentioned anionic polymers to be used as the component (B) should be the so-called "oligomers" which have a relatively low molecular weight. When the molecular weight thereof is higher, the desired sufficient dispersion stability obtained from the addition of the component (C) as mentioned hereinbelow is prevented. Contrarily, when the molecular weight is lower, the effect obtained from addition of the component (B) as mentioned hereinbelow becomes insufficient.

Specific examples of the component (B) may include one or a mixture of two or more of polyacrylic acid, polymethacrylic acid, polycrotonic acid, polyacotinic acid, poly- $\alpha$ -hydroxyacrylic acid, polymaleic acid, polysorbic acid, polyitaconic acid, poly(maleic anhydride), poly(itaconic anhydride) their copolymers, or salts of these homopolymers or copolymers.

In the liquid softener composition, the reason why excellent effect can be obtained by using the component (A) and the component (B) in combination is not clear, but it may be considered to be as follows. That is, although the ion bonding between the both may not be so strong, by forming a cation-anion complex with a part of the dispersed particles of the component (A), the component (A) can be made further hydrophobic to promote adsorption of the component (A) onto chemical fibers such as acrylic or polyester fibers which are hydrophobic fibers, whereby softness and antistatic property of the chemical fibers can be consequently further improved as compared with the case of the component (A) alone. On the other hand, the component (B) which is a water soluble polymer will not be incorporated into the dispersed particles of the component (A) and will not destroy the adsorption structure of the component (A), as different from a some kinds of anionic surfactant, and consequently will not give any adverse effect on the softness of cotton fibers.

In view of the above mechanism, it is important to control the amount of the component (B) formulated as the relative value to the component (A). Specifically, these compounds are formulated, in terms of the ratio of positive charge mols (a) of the component (A) to the negative charge mols (b) of the component (B), at a ratio (a)/(b) of 1/0.2 to 1/2.0, preferably 1/0.5 to 1/1.0. If the ratio of the component (B) to the component (A) is outside this range, the above effect of combined use is difficult to obtain.

The third essential component for accomplishing the object of the present invention is the component (C). That is, a sufficient dispersion stability is an essential condition for use as a softener for domestic use, but only with the components (A), (B), (D), the required dispersibility cannot be obtained, and accordingly the emulsifying stabilizing action of the component (C) is necessary.

The component (C) usable in the present invention may be exemplified by polyoxyethylene alkylphenyl ether, polyoxyethylene alkyl (or alkenyl) ether, polyoxyethylene fatty acid amide, polyoxyethylene alkyl (or alkenyl) amine, and polyoxyethylene sorbitane fatty acid ester. Preferable average additional moles of ethylene oxide are at least 20, more preferably 20 to 100. Examples of such a component (C) are POE ( $\bar{p}$  = 20 - 100) alkyl( $C_{8-12}$ )phenyl ether, POE( $\bar{p}$  = 20 - 100) alkyl or alkenyl( $C_{10-22}$ ) ether, POE( $\bar{p}$  = 20 - 100) alkyl or alkenyl ( $C_{10-20}$ ) amine, or mixtures thereof. In the above compounds, each POE represents

polyoxyethylene,  $\bar{p}$  denotes the average adducted moles of ethylene oxide, and C the carbon number of the alkyl or alkenyl group (hereinafter the same).

The component (C) improves the emulsifying dispersion of the dispersed particles of the component (A) alone and the anion-cation complex of the dispersed particles of the component (A) with the component (B), which may be considered to form a random coil structure dissolved in the aqueous phase in the composition, and thus the amount of the component (C) formulated is preferably 100/1 to 3/1 as a weight ratio of (A)/(C), more preferably 50/1 to 5/10. If the ratio of the component (C) to the component (A) is outside of this range, the above effect cannot be exhibited, and conversely, the above effect of combined use of the component (A) and the component (B) is frequently inhibited.

The component (D) is used as the carrier for the essential components and the optional components of the present invention, and the amount thereof in the composition is the balance which makes up the total amount to 100%, in addition to the essential components and the optional components formulated.

The softener composition of the present invention can include optional components in addition to the above essential components, including viscosity controllers such as inorganic electrolytes like sodium chloride, potassium chloride, magnesium chloride, aluminum chloride, sodium sulfate, ammonium sulfate, sodium nitrate, or magnesium nitrate; and polyethylene glycol or other water soluble organic polymers; hydrotropes such as lower alcohols like ethanol, or isopropanol, ethylene glycol, glycerine, and urea; and pH controllers, sterilizers, pigment dyes, perfumes, antioxidants, UV-ray absorbers, and fluorescent brighteners.

The softener composition of the present invention can be prepared according to known methods. More specifically, it is desirable that the component (A) should be finely and uniformly dispersed, and for this purpose, it is preferable to use the method in which the components (B), (C) and optional components are previously dissolved in an aqueous vehicle, and to this solution is successively added, under heating to 40°C to 80°C if desired, the component (A) in a molten state to be mixed under stirring. On the other hand, when optional components susceptible to denaturation at high temperature are used, it is desirable to cool the above dispersion to about room temperature, followed by addition while stirring. A pH controller can be added to the softener composition of the present invention, but the pH of the composition is not limited. Usually, the pH is that when the respective components are formulated, but it is desirable to control pH to 4 to 8. For this purpose, an organic or inorganic acid or a basic compound can be formulated, as desired.

The softener composition of the present invention which can impart an excellent softness to not only cotton fibers but also chemical fibers, and further gives an excellent antistatic property to chemical fibers is valuable.

Also it has excellent freeze-thaw stability, whereas it shows neither remarkable viscosity rise nor abnormal phase separation even when stored for a long term. Thus, the present composition is excellent in practical application.

## EXAMPLES

The present invention now will be further illustrated by, but is by no means limited to, the following examples.

The preparation, performance evaluation and dispersion stability evaluation of the softener compositions in Examples were conducted according to the following methods.

### Method of Preparation of Aqueous Dispersion:

Other components except for the component (A) were dissolved in water, the resultant solution was heated to 45°C and to this was added dropwise under stirring the molten product of the component (A) to be dispersed uniformly, followed by cooling to 25°C.

### Finishing Treatment Method:

Commercially available cotton towel, acrylic cloth were washed repeatedly twice with a commercially available detergent for clothing by means of an electric washing machine at 50°C, and then thoroughly rinsed with tap water at normal temperature to provide test cloths.

Next, into 30 liters of tap water of 25 °C was added the softener composition to an amount of the component (A) added of 1 g to form a uniform solution. Each test cloth was dipped in this solution at a bath ratio of 30-fold to carry out the treatment for 3 minutes, and then dehydrated for 2 minutes. The cloth thus treated was dried on air, and then the cotton towel for evaluation of softening effect was left to stand under the conditions of 25 °C, 65% RH for 24 hours, while the acrylic cloth for evaluation of antistatic effect under the conditions of 20 °C, 50% RH for 72 hours, before use for the respective evaluation tests.

#### Performance Evaluation Method:

(a) Softness: Touch feelings of cotton towel before and after treatment were compared and evaluated according to the following standards:

- + 5 ..... very soft
- + 4 ..... considerably soft
- + 3 ..... soft
- + 2 ..... some softness
- + 1 ..... slightly soft

0 ..... unchanged, as before treatment;

(b) antistatic property: By means of a static honestometer (manufactured by Shishido Shokai), the polyester cloth was charged at an application voltage of 7 KV at a target distance of 20 mm, and the half life (sec.) of the residual voltage after the removal of the applied voltage was measured.

#### Method of Evaluation of Dispersion Stability:

(a) viscosity change: The viscosities for each softener composition prepared, one composition immediately after preparation, one freezed at -15 °C for 40 hours and then thawed at 25 °C and one stored at 45 °C for one month were measured by means of a B type viscometer (manufactured by Tokyo Keiki) (measurement was conducted at 25 °C);

(b) judgement of phase separation: each softener composition prepared was charged into a transparent cylinder bottle of 45 mm in inner diameter to 70 mm from the bottom of the bottle, stationarily stored at 5 °C for one month, and then the separated length was measured. Evaluation:

o: not separated

Δ: separated length less than 3 mm

x: separated length of 3 mm or longer

#### Example 1

Various liquid softener compositions with various liquid properties shown below were prepared, and their performances and dispersion stabilitis thereof were evaluated. The results are shown in Table 1.

Component (A): di-hardened tallow alkyldimetyl-  
ammonium chloride: 5%

Component (B): (Polymer shown in Table 1)  
: [equivalent in charge molar ratio  
to component (A)]

Component (C): POE (p=40) nonylphenyl ether  
: 0.25% [(A)/(C) weight ratio=20/1]

Component (D): 3% aqueous ethylene glycol

: balance.

5 The above component (A) is available as a mixture with isopropanol, and therefore, the compositions were contaminated with about 1.7 (%) thereof.

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Table 1

No.	Component (B)	Performance				Dispersion stability				
		Softness		Antistatic property	Viscosity (centipoise)		Phase separation			
		Amount (%)	Cotton towel	Acrylic cloth	Acrylic cloth	Immediately after preparation		After storage (45°C, 1 month)	After restored from freezing	
Present products	Name	average (molecular weight 4,000)								
1	Polyacrylic acid		0.64	+5	+5	3 (sec)	60	220	440	o
2	"	( " 8,000)	0.64	+5	+4 - +5	10	100	260	740	o
3	"	( " 30,000)	0.64	+5	+4 - +5	13	140	990	1100	o
4	Sodium polyacrylate	( " 7,000)	0.85	+5	+4 - +5	18	50	160	200	o
5	Acrylic acid - methacrylic acid copolymer (Polymerization - 3:1) molar ratio	( " 40,000)	0.67	+5	+4 - +5	4	370	1400	1200	o
6	Acrylic acid - maleic acid copolymer (Polymerisation - 2:1) molar ratio	( " 9,000)	0.77	+5	+5	15	70	330	460	o
7	Polymaleic acid	( " 800)	0.51	+5	+5	17	65	290	550	o

Table 1 (continued)

		Performance				Dispersion stability					
		Component (B)	Softness	Antistatic property	Viscosity (centipoise)		Phase				
No.		Name	Amount (g)	Cotton towel	Acrylic cloth	Immediately after preparation	After storage (45°C, 1 month)	After restored from freezing	separation		
Present Products	8	Polycrotonic acid	( " 8,000)	0.76	+5	+5	25	280	1340	1160	0
Comparative example	9	(No addition)			+5	+4	40	230	880	730	0
	-	(untreated)			0	0	> 300	-	-	-	-

From Table 1, it can be understood that the softener compositions of the present invention have excellent performance and dispersion stability. More specifically, although considerable softness is exhibited in the case of di-hardened tallow alkyl dimethyl ammonium chloride alone, the softness and antistatic property of the acrylic cloth are clearly improved by addition of the component (B). Particularly, No. 1 and No. 5 can be appreciated to exhibit a very excellent antistatic property. Also, according to the experience of the present inventors, a rise in viscosity under the above storage conditions may be permissible up to about 1500 centipoise in commercial product value, and it can be seen that the products of the present invention satisfy this condition without causing phase separation due to the addition effect of the component (C) and the presence of ethylene glycol in the component (D).

### Example 2

Various softener compositions were prepared to a charge molar ratio (a)/(b) of the component (A) and the component (B) of 1/0.8, and their performances and dispersion stabilities thereof were evaluated. The results are shown in Table 2.



Table 2

	Component	No.	Present products						Comparative example		
			10	11	12	13	14	15			
Compo- sitlon (Z)	Di-hardened tallow alkylaimethyl- ammonium chloride		4.0	9.0	12.0	5.0	5.0	5.0			
	Polymale acid average (molecular 1500) weight		0.33	0.73	0.98	0.41	0.41	0.41			
	Component (A)										
Component (B)	POE( $\bar{p}=30$ ) octylphenyl ether		0.04	-	-	-	-	-			
	POE( $\bar{p}=50$ ) oleyl ether		-	3.0	-	-	-	-			
	POE( $\bar{p}=60$ ) tallow alkylamine		-	-	2.4	-	-	-			
	POE( $\bar{p}=40$ ) sec-alkyl ether ( $C_{12} - C_{14}$ )		-	-	-	0.1	0.44	2.0			
Component (D)	Ethylene glycol		5.0	6.0	10.0	4.0	4.0	4.0			
	Sodium chloride		-	0.2	0.4	-	-	-			
	Acetic acid		-	-	0.05	-	-	-			
	Deionized water		balance	balance	balance	balance	balance	balance			
Component (A)/Component (C) ratio			100/1	3/1	5/1	50/1	125/1	2.5/1			

Table 2 (continued)

	No.	Present products					Comparative example	
		10	11	12	13	14	15	
Per- formances	Softness	+5	+5	+5	+5	+5	+4 - +5	
	Acrylic cloth	+5	+5	+5	+5	+5	+3 - +4	
	Antistatic property (sec)	13	18	9	15	16	35	
Dis- persion sta- bility	Viscosity (centipoise)	320	80	150	280	450	15	
	Immediately after preparation							
	After stored (45°C, 1 month)	1440	360	680	940	3300	80	
	After restored from freezing	1300	720	870	1180	2860	130	
	Phase separation	0	0	0	0	0	x	

From Table 2, it can be understood that all of the products of the present invention have good performances and also excellent dispersion stability. In contrast, as shown in Comparative examples, if the ratio of the component (C) relative to the component (A) is too low, i.e., outside the range defined in the present invention (No. 14), viscosity elevation after a lapse of days for storage is marked, while if it is too much (No. 15), phase separation is liable to occur, and there is also an undesirable tendency that the performance to be improved by addition of the component (B) is contrariwise inhibited.

### Example 3

Using dioleoyldimethylammonium chloride as the component (A) and varying the amount of polyacrylic acid formulated as the component (B), softener compositions shown below were prepared and their performances were evaluated. The results are shown in Table 3:

Component (A): dioleoyldimethylammonium chloride  
(iodine value = 73): 9 (%);

Component (B): polyacrylic acid (average molecular weight = 1,000): 0 to about 2.3 (%);

Component (C): POE (p=50) oleylamine  
: 2 (%) [(A)/(C) weight ratio=4.5/1];

Component (D): sodium chloride: 0.2 (%)  
: glycerine: 10 (%)  
: deionized water: balance

The above component (A), is provided as a mixture with isopropanol, and therefore, the compositions were contaminated with about 3 (%) thereof.

Table 3

	No.	Amount of the component (B) (%)	Component (A)/Component (B) charge molar ratio (a)/(b)	Performance evaluation results		
				Softness		Antistatic property
				Cotton towel	Acrylic cloth	Acrylic cloth
Comparative example	16	(no addition)	1/0	+3	+3	100 (sec)
Present products	17	0.11	1/0.1	+3	+3	80
	18	0.23	1/0.2	+3	+3	50
	19	0.57	1/0.5	+3	+3 - +4	15
	20	0.91	1/0.8	+3 - +4	+3 - +4	3
	21	1.14	1/1.0	+3 - +4	+3 - +4	2
	22	1.71	1/1.5	+3	+3 - +4	30
	23	2.29	1/2.0	+3	+3	70
	24	2.86	1/2.5	+3	+3	90

From Table 3, it can be understood that softness and/or antistatic property of the acrylic cloth can be improved by an addition of the component (B). Furthermore, it is also clear that the softness of the cotton

towel is improved in some cases. Thus, these effects are more marked when the charge molar ratio (a)/(b) is within the range from 1/0.2 to 1/2.0, more preferably from 1/0.5 to 1/1.0. Also all of the above compositions of the present invention have a good dispersion stability, which may be attributed to the addition effects of the component (C) and glycerine in the component (D).

#### Example 4

Using various slightly water soluble di/tri-long chain alkyl/alkenyl quaternary ammonium salts as the component (A) and sodium polyacrylate as the component (A) at equivalent charge molar ratio (a)/(b), softener compositions with the compositions shown below were prepared and their performances were evaluated and compared with the case when sodium polyacrylate was not added. The results are shown in Table 4.

Component (A): (quaternary ammonium salt listed in Table 4)

: 5.0 (%);

Component (B): sodium polyacrylate (average molecular weight 7000)

: 0 (%) or amount to charge molar ratio (a)/(b) of 1/1;

Component (C): POE (p=20) branched alkyl ether (C<sub>13-15</sub> branching ratio 50%)

: 0.4 (%)

[(A)/(C) weight ratio=12.5/1]

Component (D): propylene glycol: 6.0 (%)

deionized water: balance

Table 4

	No.	Composition		Performances		
		Name of component (A)	Amount of component (B) (%)	Softness		Antistatic property
				Cotton towel	Acrylic cloth	
Present products	25	Diolelyldimethylammonium chloride	0.82	+3	+3 - +4	3 ( )
	26	Di(methyl branched isostearyl)dimethylammonium chloride	0.80	+3 - +4	+4	2
	27	Dioleylmonostearyl ammonium chloride	0.59	+3 - +4	+4 - +5	4
	28	Di-hardened tallow alkylemethyl ammonium chloride POE( $\bar{p}=3$ )	0.69	+4 - +5	+3 - +4	4
	29	Di(2-tallow amidoethyl)methyl ammonium chloride POE( $\bar{p}=2$ )	0.61	+3	+3	44
	30	Di(2-palmitoylethyl)hydroxyethylmethylammonium methylsulfate	0.69	+3	+3 - +4	58
	31	Methyl-tallow amidoethyl-2-tallow imidozolinium methyl sulfate	0.65	+3 - +4	+4	6
Comparative example	32	(the same as No. 25)	0	+3	+3	100
	33	(the same as No. 25)	0	+3 - +4	+3 - +4	75
	34	(the same as No. 27)	0	+3 - +4	+3 - +4	43

Table 4 (continued)

	No.	Composition		Performances			
		Name of component (A)	Amount of component (B) (%)	Softness		Antistatic property	
				Cotton towel	Acrylic cloth	Cotton towel	Acrylic cloth
Comparative example	35	(the same as No. 28)	0	+4 - +5	+4	25	
	36	(the same as No. 29)	0	+2	+2	220	
	37	(the same as No. 30)	0	+2	+3	140	
	38	(the same as No. 31)	0	+3 - +4	+3	110	

From Table 4, it can be understood that the carboxylic acid type anionic polymers used in the present invention have performance improvement effects on all of the slightly water soluble quaternary ammonium salts having different structures from each other. More specifically, in Table 4, it can be seen that by an addition of sodium polyacrylate in equivalent amount to the component (A), in all cases, the performances,

particularly softness and antistatic property of the acrylic cloths are greatly improved. Also, all of the above compositions of the present invention have good dispersion stability.

## 5 Claims

1. A liquid softener composition comprising:

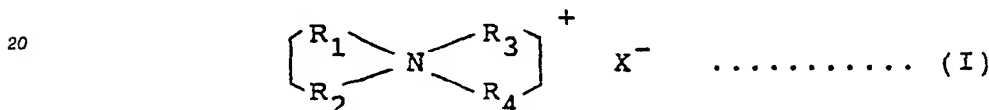
(A) a slightly water-soluble quaternary ammonium salt cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;

10 (B) a carboxylic acid anionic polymer;

(C) a polyoxyethylene adducted nonionic surfactant; and

(D) an aqueous vehicle, with the weight ratio of the components (A)/(C) being within range of from 100/1 to 3/1.

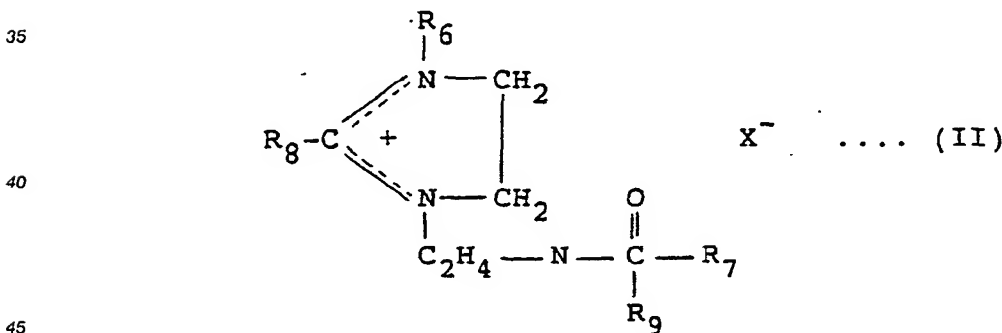
15 2. A liquid softener composition as claimed in claim 1, wherein said slightly water-soluble quaternary ammonium salt cationic surfactant (A) is at least one component selected from the group consisting of the cationic surfactants having the formulae (I) and (II):



25 wherein at least two groups  $R_1$  through  $R_4$  represent straight or branched alkyl or alkenyl groups which may be unsubstituted or optionally substituted with

$-\text{OH}$ ,  $-\text{O}-$ ,  $-\text{C}(=\text{O})-\text{NH}-$ , or  $-\text{C}(=\text{O})-\text{O}-$ ,

the remainder of the groups of  $R_1 - R_4$  represent an alkyl group with 1 to 3 carbon atoms, a hydroxyalkyl group or a group represented by the formula  $-(\text{C}_2\text{H}_4)_t\text{H}$  where  $t$  is an integer of 1 to 5, and  $X$  represents a halogen or a monoalkylsulfate group represented by  $\text{R}_5\text{SO}_4$  where  $\text{R}_5$  represents an alkyl group with 1 to 3 carbon atoms.



wherein  $\text{R}_6$  represents an alkyl group with 1 to 4, preferably 1 to 2 carbon atoms,  $\text{R}_7$  and  $\text{R}_8$  each represent an alkyl or alkenyl group with 14 to 24 carbon atoms,  $\text{R}_9$  represents hydrogen or an alkyl group with 1 to 4 carbon atoms, and  $X$  has the same meaning as in the formula (I).

50 3. A liquid softener composition as claimed in claim 1, wherein the amount of the component (A) is 3 to 50% by weight.

4. A liquid softener composition as claimed in claim 1, wherein said carboxylic acid anionic polymer (B) is at least one polymer selected from the group consisting of homopolymers of ethylenically unsaturated carboxylic acids and anhydrides thereof and their copolymers and salts of said homopolymers and copolymers.

55 5. A liquid softener composition as claimed in claim 1, wherein said carboxylic acid anionic polymer (B) has an average molecular weight of 500 to 50000.

6. A liquid softener composition as claimed in claim 1, wherein the ratio of the components (A)/(B), in terms of positive charge mol (a) of component (A)/negative charge mol (b) of component (B), of 1/0.2 to 1/2.

7. A liquid softener composition as claimed in claim 1, wherein the average adducted moles of ethylene oxide of the component (C) is at least 20.

5 8. A liquid softener composition as claimed in claim 1, wherein the weight ratio of the components (A)-(C) is 50/1 to 5/1.

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⑤④ **Liquid softener composition.**

⑤⑦ A liquid softener composition comprising:

(A) a slightly water-soluble quaternary ammonium salt type cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;

(B) a carboxylic acid type anionic polymer;

(C) a polyoxyethylene adducted nonionic surfactant; and

(D) an aqueous vehicle, wherein the weight ratio of (A)/(C) is within range of from 100/1 to 3/1.

**EP 0 335 404 A3**



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 89 10 5663

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2459125 (CIBA-GEIGY AG) * claims 1, 8, 10 * ---	1-2	C11D1/835 C11D3/37
A	US-A-3537993 (T.L. COWARD ET AL.) * column 1, line 10 - column 3, line 17 * * column 4, lines 63 - 70 * ---	1-4, 7	
A	FR-A-2407261 (UNILEVER) * page 4, line 10 - page 5, line 33; claim 1 * ---	1-2, 4-5, 7	
A	GB-A-2151252 (SANDOZ LTD) * claims 1, 3 * -----	1, 4-5, 7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 OCTOBER 1990	Examiner SERBETSOGLU A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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**C1H1X C1H2A C1H2C**

**C1H3A C1H3C C1J C1L4**

**C2A12A10 C2A12A7**

**C2A12A8 C2A12AX**

**C2A12B1 C2A12BX**

**C2C6 C2CX**

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(58) Field of search

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(54) **Treatment of textiles**

(57) A method of treating textiles comprises applying to the textile a water-soluble curable polymeric material in an aqueous medium, simultaneously or subsequently applying to the textile a compatible exhaustion agent which reduces the solubility of the polymeric material, allowing the polymeric material to exhaust onto the textile and curing the polymeric material.

GB 2 005 322 A

## SPECIFICATION

## Treatment of textiles

- 5 This invention relates to the treatment of textiles, in particular with water soluble polymeric materials. 5

Polymeric materials such as the Bunte salt compounds disclosed in our British Patent No. 1,423,342 or the poly(carbamoylsulphonates) disclosed in British Patent No. 1,419,306 are especially suitable as textile finishing agents, in particular in conferring shrink resistance on

- 10 keratinous textile materials such as wool. 10

Such resins have hitherto been applied to textile piece goods principally by means of pad mangles. Pad mangles are relatively expensive and not at all textile finishers have one. Accordingly, the invention seeks to provide a process of finishing textiles, from either short or long liquors, which may be carried out in widely available wet processing equipment following a

- 15 simple processing route and using only inexpensive auxiliary chemicals. 15

According to the present invention there is provided a method of treating textiles which comprises applying a water-soluble curable polymeric material, optionally in the presence of alkali, in an aqueous medium to the textile, simultaneously or subsequently applying a compatible exhaustion agent, allowing the polymeric material to exhaust onto the textile, and

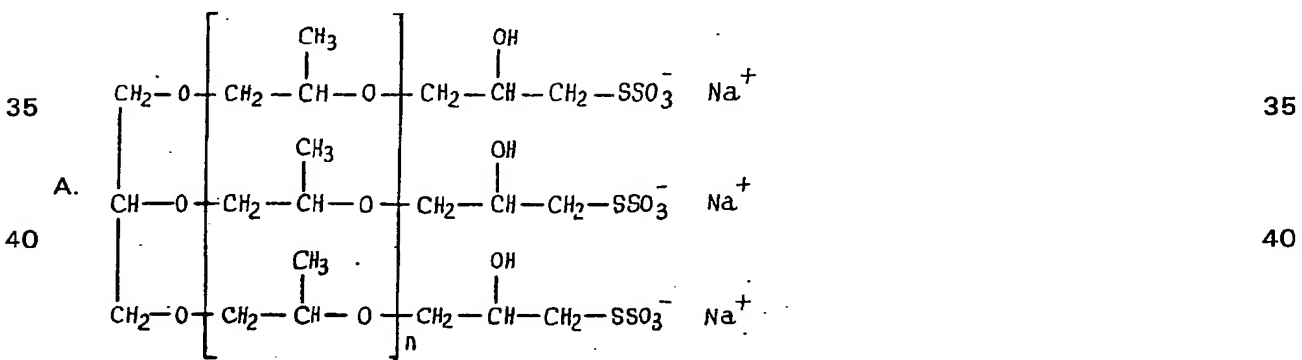
- 20 curing the polymeric material. The term 'curing' includes allowing to cure. 20

The process is generally applicable to water-soluble curable polymers and especially those having ionic charges. Examples of suitable polymers include polycarbamoyl sulphonates, Bunte salt polymers, the amphoteric polymers of our British Patent Application No. 9467/75, anionic acrylate emulsions, cationic polymers such as polyamide-epichlorhydrin polymer, azetidinium

- 25 polymers, and blocked polyisocyanate emulsions (made ionic by addition of an anionic surfactant). 25

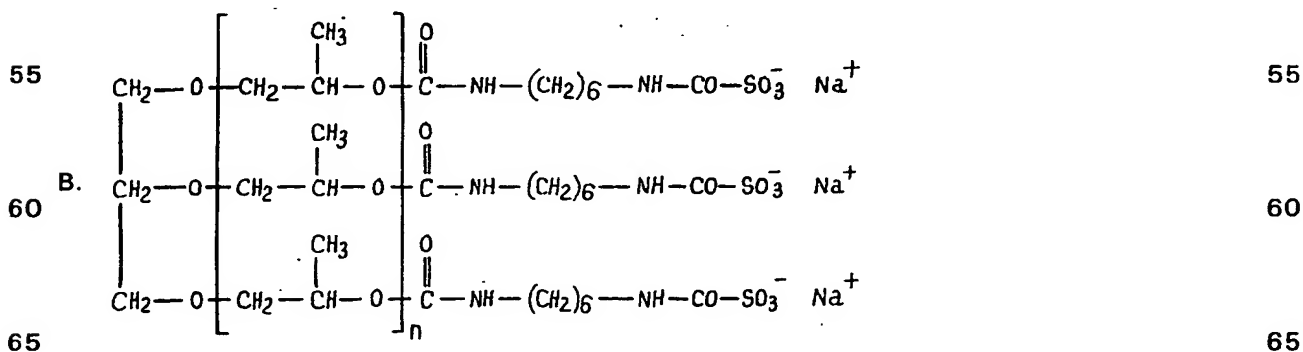
Preferred curable polymeric materials have a polymeric chain backbone and at least two thiosulphate groups per molecule. The chain may advantageously be a polyoxyalkylene, e.g. polyoxypropylene, chain. Particularly preferred materials of this type have the following

- 30 structural formula: 30



where n is about 13.

Other polymeric materials useful in the process of the invention include poly(carbamoylsulphonates). These may conveniently be prepared from polymeric di- or poly-isocyanates by treatment with sodium bisulphite. Preferred poly(carbamoylsulphonates) have polyoxyalkylene, e.g. polypropylene, backbones and three carbamoylsulphonate groups. Particularly preferred poly(carbamoylsulphonate) have the following formula:



where n is about 13.

In general, the amount of polymeric material applied will be between  $\frac{1}{2}$  and 10% on the weight of the fibres (o.w.f.), with amounts in the range of 2 to 4% o.w.f. being preferred.

- 5 Curing routes for the polymer include: removing the goods from the treatment bath after exhaustion and curing at high temperature (e.g. 120 to 160°C), preferably in a stenter; or removing the goods after exhaustion, drying them at, say, 50°C, and then steaming them to effect curing. 5

- Alkalies promote cross-linking or curing of the polymeric material. It is frequently advantageous to pre-mix an alkali with the polymeric material for an ageing period to provide a partially cross-linked, or activated, polymer before application to the textile. This is particularly advantageous when operating at short liquor ratios. Typically ageing periods of 10 to 60 minutes may be employed. At long liquor ratios it may be advantageous to raise the pH of the liquor by addition of alkali at or towards the end of the exhaustion to promote curing although this is not essential and curing by other methods such as heat curing is possible. Any alkali may be used, for example 10  
15 alkali metal carbonates or hydroxides, but particularly good results are obtained using ammonium hydroxide or, at short liquor ratios, trisodium phosphate. 15

- When alkali is used the amount of alkali present is advantageously sufficient to ensure an alkaline reaction of the treatment liquor, preferably a pH value of 8 to 10. In a long liquor it is desirable to ensure that the weight of alkaline compound present or added is sufficient to achieve an alkaline reaction on the textile, which may contain residual acid from a previous process, for example carbonization. 20

- The exhaustion agent may be any soluble compound which reduces the solubility of the polymeric material and does not react adversely with the other compounds present and is preferably ionic in character, especially an inorganic salt. In general, any neutral metal salt may be used. Particularly useful are alkali metal, alkaline earth or ammonium salts of strong acids, 25  
e.g.  $\text{Na}_2\text{SO}_4$ , NaI, NaCl,  $\text{MgSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$  and especially  $\text{MgCl}_2$ . It appears that salts of divalent metals are twice as effective, on a weight basis, as salts of monovalent metals. The amounts required vary with the nature of the compound, but in general between 1 and 100 g/l preferably 5 to 10 g/l may be used. Trivalent or polyvalent salts, e.g.  $\text{AlCl}_3$  or  $\text{FeCl}_3$ , may 30  
be used but, since they act very quickly, care must be taken to ensure level treatments. 30

The process of the invention can be applied using long or short liquors. When using short liquors, typically 1:1 to 3:1, the liquor is virtually completely absorbed by the textile goods. The preferred processing sequence is as follows:

- (i) the polymeric compound and an alkali are mixed and allowed to age;  
35 (ii) the liquor from (i) is applied to the goods in a washing machine or milling machine;  
(iii) the goods are agitated until a uniform distribution of the liquor is obtained;  
(iv) a solution of inorganic salt is sprayed onto the goods and agitation continued until it is evenly distributed; and  
(v) the goods are rinsed, hydroextracted and dried.  
40 In order to avoid any risk of slight discoloration of the goods being treated it is preferred to add a mild bleaching at a late stage in the process. Suitable agents include oxidising agents such as hydrogen peroxide, and reducing agents such as bisulphites. 40

- No separate curing step is needed since the polymer is fully cured at the end of step (iv). Furthermore, the process can be carried out at room temperature and so energy costs are kept 45  
to a minimum. 45

- In order to check that the liquor is evenly distributed at the end of steps (iii) and (iv) sighting colours may be used. For example, a pink sighting colour added to the initial liquor will colour the goods a level pink colour when step (iii) is completed. If a blue sighting colour is added with the salt solution the end of step (iv) can be ascertained when the goods are an even purple 50  
colour. Both sighting colours will wash out completely during the rinsing step. 50

- The short liquor ratio process can be carried out in any short liquor processing apparatus capable of agitating the goods, preferably with a tumbling action. Washing machines are especially suitable. For knitwear, e.g. Shetland sweaters, which is generally subjected to a milling operation, the process may be carried out in the milling machine.

- 55 When the process is applied using long liquors, typically at liquor ratios from 10:1 up to, say, 100:1, and especially in the range 20:1 to 30:1, suitable machinery includes side-paddle machines, winch machines, beam machines and dolly washers. The preferred processing sequence for long liquor ratios is as follows: 55

- (i) the polymer is added to the bath containing the goods set at a pH between 5 and 8;  
60 (ii) a solution of the inorganic salt is added and the temperature raised to 50°C;  
(iii) after exhaustion is complete (usually in 30 to 60 minutes) alkali is added to pH 9-10;  
and  
(iv) after a further 15 to 30 minutes the goods are hydroextracted and dried;  
This sequence involving steps (iii) and (iv) allows the goods to be dyed in the same bath  
65 without intermediate drying, thus saving a processing step. 65

Thus it can be seen that both long and short liquor processes may be carried out simply using common and inexpensive chemicals in widely available apparatus using a short and simple treatment cycle.

- 5 While the process may be used in finishing textiles generally it is especially applicable to  
textiles of keratinous fibres such as wool. With the latter, resistance to area felting shrinkage  
during subsequent laundering is conferred. 5

The process is applicable to textiles in forms varying from loose stock, sliver, top and yarn to piece goods and garments. It has been found particularly useful with knitted piece goods and garments, especially Shetland or lambswool knitwear.

- 10 When long liquors are employed, it will be observed that, as the temperature approaches  
50°C, the polymer/salt solution becomes milky in appearance, whereas if the temperature is  
increased it goes clear again. Best results are obtained when carrying out the process at or near  
the temperature of maximum turbidity. 10

- 15 It is preferred that the goods should be free from dirt, grease or spinning oils and therefore  
pre-scouring in a detergent solution, preferably non-ionic, is recommended. Similarly a non-ionic  
or anionic detergent may be added to the liquor to ensure complete wetting-out of the goods  
during processing. 15

The following Examples are given to illustrate the invention. The preparation or origin of the polymeric compounds employed in Examples 8 to 60 are as follows.

- 20 20

#### *Preparation of Amphoteric Polymers*

Two polymers were prepared in accordance with the disclosures of our British Applications Nos. 9467/75 and 28569/77, one using the H<sub>2</sub>SO<sub>4</sub> route and a second using the toluene sulphonic acid route. These are designated APS I and APS II respectively.

- 25 25

#### *Preparation of APS I*

- 67.5 g of synthappret LKF (an 80% solids isocyanate-terminated prepolymer—Bayer A.G.)  
were dissolved in 25 g of dry ethyl acetate. 1.57 g H<sub>2</sub>SO<sub>4</sub> (A.R. 100%) was added and the  
reaction mixture stirred for 45 minutes. 50 g isopropyl alcohol, 12.5 g dioxan and 4.5 g of  
30 sodium metabisulphite dissolved in 15 cm<sup>3</sup> water were then added. The reaction mixture was  
brought to pH 5 with the addition of 0.5 g sodium dicarbonate. The reaction was followed  
spectrophotometrically. The product was acidified with 5 g HCl (conc.). Analysis of the product  
showed it to contain 57% cationic groups and 43% anionic groups. 30

- 35 35

#### *Preparation of APS II*

- 150 g of Synthappret LKF were dissolved in a 16 g dioxan—4 g ethylacetate mixture. 8 g of  
dried toluene sulphonic acid monohydrate was added with stirring, reaction being complete in  
25 minutes 150 g isopropyl alcohol and 9 g of sodium metabisulphite, dissolved in 70 cm<sup>3</sup>  
water, were added to the reaction mixture. The reaction mixture was brought to pH 5 with 3 g  
40 sodium bicarbonate and stirred continuously. The reaction was followed spectrophotometrically.  
On completion the product was acidified with 15 g HCl. Analysis showed the product to contain  
55% cationic groups and 45% anionic groups. 40

#### *Preparation of Acetone Oxime Blocked Polyisocyanate*

- 45 300 parts by weight (0.1 mole) of a 3000 molecular weight polypropylene oxide triol were  
dried by heating under vacuum for 30 minutes at 120°C. After cooling and blanketing the  
polyol with nitrogen, 57.4 parts by weight (0.33 mole) of 2,4-toluene diisocyanate were added  
and the temperature of the reaction mixture was maintained at 75°C until analysis of the  
reaction mixture showed that 45.5% of the isocyanate groups originally present had reacted.  
50 The polyisocyanate was then cooled to 35°C and 26.3 parts by weight (0.36 moles) of acetone  
oxime were added and the mixture stirred to dissolve the acetone oxime. Stirring was continued  
until infra-red analysis indicated that all the isocyanate groups present had reacted with the  
acetone oxime. 50

- The adduct was diluted to an 80% solution by the addition of 106 parts by weight of toluene.  
55 An aqueous emulsion of this product was prepared by dissolving 10 parts by weight of Atlab  
Test Surfactant HLB 10 (Honeywill Atlas) in 100 parts by weight of the solution of the blocked  
polyisocyanate. This solution was transferred to a high shear mixer and 210 parts by weight of  
water were added whilst mixing with high shear to form a 25% solids emulsion of the blocked  
polyisocyanate. 60

- 60 60

#### *Other Polymeric Preparations*

"Impranil DLH" is an anionic aliphatic polyester urethane dispersion free from organic solvents and emulsifiers, supplied by Bayer AG as a 40% aqueous dispersion. "Impranil DLN" and "Impranil 4693" are of similar constitution.

- 65 Polyacrylate E 1070 is a self cross-linking polyacrylate emulsion supplied by Rohm and Haas 65

(UK) Ltd. as a 46% aqueous emulsion.

Hercosett 57 is a polyamide-epichlorohydrin resin supplied by Hercules.

The bisulphite addition product (BAP) of Synthappret LKF was prepared by known techniques, as described in British Patent No.

5 The amount of polymer applied is indicated in % on the weight of wool (oww). 5

#### Wash Test

In the Examples, fabric samples were wash tested in a 'Cubex' washing machine in 15 litres of pH 7 phosphate buffer solution at 40°C with a 1 kg load including, where necessary, 10 makeweights. Area felting shrinkage results are given as percentage change in area after 1 hour 10 or 3 hours washing.

#### Example 1

Unscoured Shetland wool swatches (2/8's worsted count yarn; knitted to cover factor 0.85) 15 (1 kg) were prescoured in a Wascator washing machine using a solution containing a non-ionic detergent (Lissapol NX, ICI) 2 g/l, sodium sulphate 2 g/l and sodium metabisulphite 2% o.w.f. 15 Scouring was carried out at 40°C for 10 min.; the goods were then rinsed well and hydroextracted to 50% pick-up.

An activated emulsion of Bunte salt polyether polymer was prepared by dissolving trisodium 20 phosphate (30.0 g) in 1,920 ml of water and then adding 80 ml of a Bunte salt polyether 20 (Lankrolan SHR<sub>3</sub>, Lankro Chemicals Ltd.) (40% solids) (i.e. 16 g/l Bunte salt polymer, 15 g/l Na<sub>3</sub>PO<sub>4</sub>). Duratint Pink (5 g/l) was also added at this stage. This solution was allowed to age for 30 minutes before adding to the prescoured wool goods. (Allowing for the water remaining on the goods from prescouring this give a liquor ratio of 2.5:1).

25 The addition of the activated polymer emulsion to the goods in the Wascator machine may be 25 made either by spraying directly onto the goods with the machine switched on to give a tumbling action, or simply by pouring onto the bulk of the material prior to tumbling. In this Example, tumbling was carried out for thirty minutes during which time the pink tinted solution rapidly redistributes itself evenly along the knitted swatches; even those swatches which were 30 quite white at the start of the tumbling cycle were observed to be evenly tinted showing that the 30 liquor had distributed itself evenly.

At this point 500 ml of a blue tinted 6% (w/v) solution of sodium chloride was added to the Wascator, again either by spraying or simply by pouring onto the bulk of the swatches. (The effective liquor ratio was then 3:1).

35 Tumbling was carried out for a further 15 min., when it was seen that all the swatches were 35 uniformly pre-tinted. The swatches were then rinsed with cold water to remove both the tints and the inorganic salts. Hydroextraction and drying completed the process.

Three sample swatches were taken from the front, centre and back of the machine and without drying were subjected to the 15-litre Cubex wash test. The following results were 40 obtained:- 40

45 Sample	% Area shrinkage		45
	1 hour wash	3 hour wash	
Front of machine	- 2	0	
Centre of machine	1	1	
Back of machine	- 3	- 1	
50 Scoured only	35	61	50

Negative values indicate an extension

#### Example 2

55 The procedure of Example 1 was essentially followed, except that processing was carried out 55 in a "Cherry Tree" milling machine commonly used for milling woollen garments. Again, good machine washability without intermediate drying was obtained.

#### Example 3

60 An all wool woven worsted 2/2 twill fabric was scoured in the usual way and then placed in 60 a conventional fabric milling machine. An activated ( $\frac{1}{2}$  hour aged) liquor (16 g/l Lankrolan SHR<sub>3</sub>, 15 g/l trisodium phosphate) was prepared as in Example 1 and 100 kg added slowly by pouring directly onto the moving fabric (40 kg). The pressure on the throat of the milling machine was adjusted so that after 15 minutes 6% width shrinkage had occurred. After this 65 time the pressure was relaxed and after running for a further 15 minutes it was seen that level 65

distribution of the liquor over the fabric had been produced. At this stage 50 kg of a 6% sodium chloride solution was added and the fabric run a further fifteen minutes under very little throat pressure. Rinsing with water, hydroextraction and drying completed the process.

Cubex testing (15 litre, 3 hours) gave zero area shrinkage compared with 43% for the untreated fabric.

#### Example 4

Shetland fabric (2/8's worsted count yarn knitted to cover factor 0.85) was scoured and milled in Lissapol NX (2 g/l) and anhydrous sodium sulphate (2 g/l). The wool was then rinsed. In a fresh bath at 20°C and 30:1 liquor ratio, 1.5 g/l 0.880 ammonia was added followed 5 minutes later by 3.5% (solids) o.w.f. Lankrolan SHR 3. 15 g/l sodium chloride was then added and the whole raised to 50°C over 10 min. Exhaustion to about 90% occurred over 30 min. whereupon a further 5 g/l sodium chloride was added and circulation continued for a further 30 min. At this stage the wool passed the I.W.S. Superwash (TM 185) felting shrinkage test (1st hour 0%; 2nd hour 1%; 3rd hour 2%). However, it was conventionally hydroextracted and tumble dried at 90°C for 15 min., when the shrinkage figures were found to be similar to those of the undried fabric.

#### Example 5

The Shetland fabric of Example 4 was scoured and milled. A stock solution was made up containing 80 g/l Lankrolan SHR3 and 20 g/l ammonia. This was aged for 30 min. The scoured and milled wool was wetted out at a liquor ratio of 30:1 at 20°C and the bath brought to pH 9 by the addition of ammonia. The resin stock was then added to a dosage level of 3.5% o.w.f. resin solids followed by 15 g/l sodium chloride. The bath was raised to 50°C and circulated for 30 min. A further 5 g/l sodium chloride was then added and circulation continued for 30 min.

The goods were then hydroextracted and tumble dried (90°C, 15 min.) and Cubex tested:-

	1 hour	2 hour	3 hour
Area shrinkage: —	1	3	5

If Cubex testing is carried out before drying, equally good results are recorded, indicating that polymer crosslinking occurs on the fabric before drying.

#### Example 6

A worsted serge fabric was treated on a winch machine by the method of Example 2. After hydroextraction and drying, the fabric was Cubex tested and found to give an area shrinkage value (3 hour, 15-litre test) of 0%. The untreated fabric gave a value of 43%.

#### Example 7

Shetland wool samples are scoured and milled as in Example 4. The procedure of Example 4 was then followed except that 10 g/l magnesium sulphate was added instead of the sodium chloride. The pH of the treatment liquor was 9.5. The temperature was raised to 50°C over 10 min. and then held at 50° for 5 min., whereupon 2% o.w.f. of sodium metabisulphite was added and the bath run a further 15 min. at the same temperature.

The samples were then hydroextracted and the following wash test results obtained on samples which had been air dried or tumble dried.

	Area shrinkage %		
	1 hour wash	2 hour wash	3 hour wash
Air dried	1	2	3
Tumble dried	0	0	1

#### Examples 8-10

The fabric was a plain weave unbleached woollen flannel fabric of weight 185 g.m<sup>-2</sup>. It was scoured with 1 g/l non-ionic detergent (Lissapol N, ICI) and 2 g/l Na<sub>2</sub>CO<sub>3</sub> at 40°C for 10



minutes, followed by rinsing.

Samples of the fabric were run in a bath of liquor ratio 40:1 set at 50° and pH 7, containing 2.0% (solids) owv BAP and 10 g/l of either of the following metal salts: MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>. The temperature was maintained at 50°C until exhaustion took place. The wool was then either

(i) rinsed and dried at 140° for 15 minutes (heat cure),

(ii) dried at 50°C for 15 minutes and steamed 5 minutes (steam cure), or

(iii) cured in the treatment bath by raising the pH to 9 and holding for 30 minutes followed by drying at 50°C for 15 minutes (bath cure).

Example No	Metal salt	Time to Exhaustion (min.)	Area Shrinkage (%)					
			Heat Cure		Steam Cure		Bath Cure	
			1 hr	3 hr	1 hr	3 hr	1 hr	3 hr
8	MCl <sub>2</sub>	35	3	11.5	2	8	3	5
9	CaCl <sub>2</sub>	20	9.5	25	8	19	4	12
10	ZaSO <sub>4</sub>	180	4	19	3.5	15	4	11
Untreated fabric			1 hr wash 32%, 3 hr 45%					

#### Examples 11-13

Samples of scoured flannel were run in a bath of liquor ratio 40:1 set at pH 7 and 50°C, containing 1% (solids) owv BAP, 1% (solids) Impranal DLH and 10 g/l of one of the following metal salts: MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>.

The temperature was maintained at 50°C until exhaustion took place. The polymers were then cured as in Examples 8-10.

Example	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)					
			Heat Cure		Steam Cure		Bath Cure	
			1 hr	3 hr	1 hr	3 hr	1 hr	3 hr
11	MgCl <sub>2</sub>	25	4.5	18	4	10	1.5	5
12	CaCl <sub>2</sub>	12	10	25	4	13	4	15
13	ZnSO <sub>4</sub>	90	4	175	6	20	7	24

#### Examples 14-19

Samples of flannel were run in a bath of liquor ratio 40:1 set at 50°C and pH 7, containing either 4.0% (solids) owv APS I or 4.0% (solids) owv APS II and 10 g/l of one of the following metal salts; MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>. The temperature was maintained at 50°C until exhaustion

took place. Samples were then cured as in Examples 8-10.

50	Example	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)						50
				Heat Cure		Steam Cure		Bath Cure		
				1 hr	3 hr	1 hr	3 hr	1 hr	3 hr	
APS I										
55	14	MgCl <sub>2</sub>	15	7	27	2	13	1	8	55
	15	CaCl <sub>2</sub>	15	3	24	2	20	3.5	18	
	16	ZnSO <sub>4</sub>	25	2	8	3.5	10	0	1	
APS II										
60	17	MgCl <sub>2</sub>	30	5	25	0	9	0	7	60
	18	CaCl <sub>2</sub>	30	4	28	0	11	2	10	
	19	ZnSO <sub>4</sub>	45	0	5	1	5	0	0	

#### Examples 20-22

Samples of scoured flannel were run in a bath of liquor ratio 40:1 set at pH 7 and 50°C

containing 4.0% (solids) acetone oxime blocked polyisocyanate, 0.5 g/l sodium lauryl sulphate and 10 g/l of one of the following metal salts:  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ . The temperature was maintained at 50°C until exhaustion was complete. The polymer was cured either by:

- (i) heating the sample to 140°C for 15 minutes, or  
 (ii) drying at 50°C for 15 minutes followed by steaming for 5 minutes.

Example No	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)			
			Heat Cure		Steam Cure	
			1 hr	3 hr	1 hr	3 hr
20	$\text{MgCl}_2$	45	0	1	0	1.5
21	$\text{CaCl}_2$	45	2	6	2	2.5
22	$\text{ZnSO}_4$	60	0	1	0	7

#### Examples 23-24

The procedure of Example 8 was repeated using 5% (solids) oww of E 1070 polyacrylate followed by heat curing at 150°C for 15 minutes. The results appear below:

Example No	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)	
			1 hr	3 hr
23	$\text{MgCl}_2$	60	0	6
24	$\text{CaCl}_2$	80	0	14

#### Examples 25-27

The procedure of Example 8 was repeated using Hercosett 57 (Hercules) polyamide-epichlorohydrin resin together with an anionic exhaustion agent, sodium hexametaphosphate, commercially available as Calgon PT. Heat curing at 140°C for 15 minutes was used. The results appear below:

Example No.	% of Hercosett 57 oww	Time to Exhaustion (min.)	Area Shrinkage (%)	
			1 hr	3hr
25	10	45	1	6
26	8	25	2	7
27	6	30	5	11

#### Examples 28-33

In order to determine the effect of concentration of metal salt, Example 11 was repeated using different concentrations of  $\text{MgCl}_2$ . In each case the fabric was dried and heat cured at 140°C for 15 minutes.

5	Example No.	MgCl <sub>2</sub> Conc.	Time to Exhaustion (min.)	Area Shrinkage (%)		5
				1 hr	3 hr	
	28	4	60	0	0	
	29	5	40	0	0	
	30	6	30	0	0	
10	31	7	20	1	3.4	10
	32	8	15	1.4	5.5	
	33	10	12	0.4	6.4	

15 It can be seen that the rate of exhaustion is controlled by the concentration of MgCl<sub>2</sub>. Rapid exhaustion times are generally not preferred since the washability and handle of the treated goods may not be up to the standard obtainable with more controlled exhaustion. 15

#### Examples 34-38

20 Examples 28 to 33 were repeated using 7 g/l MgCl<sub>2</sub> and varying the temperature of the bath. Heat curing was employed as before. The results of wash tests are given below. 20

25	Example No.	Bath Temperature	Time to Exhaustion (min.)	Area Shrinkage (%)		25
				1 hr	3 hr	
	34	30°	50	0	5	
30	35	40°	35	0	5.3	30
	36	50°	20	0.5	3.5	
	37	60°	16	1	2.5	
	38	70°	12	1	6.4	

35 Examples 39-43 35

Examples 28 to 33 were repeated using different ratios of BAP/Impranil DLH applied across the range. 2.0% BAP/0% DLH to 0% BAP/2% DLH with 2% total solids applied. Exhaustion time was maintained constant (at 45 min.) by varying the MgCl<sub>2</sub> concentration according to ratio of polymers. Curing was by dry heat at 140°C for 15 minutes. The results of wash tests were as follows: 40

45	Example No.	% BAP oww	% DLH oww	MgCl <sub>2</sub> conc. g/l	Area Shrinkage (%)		45
					1 hr.	3 hr	
	39	2.0	0	9.0	0	1	
	40	1.5	0.5	7.0	1.5	0.5	
	41	1.0	1.0	6.0	1	1	
50	42	0.5	1.5	3.0	0.5	1	50
	43	0	2.0	3.5	9.8	30.3	

#### Examples 44-47

55 Examples 28 to 33 were repeated on knitted fabric. The fabric used was single jersey wool fabric knitted from 2/24's worsted yarn to a cover factor of 1.1. It was scoured with 1 g/l non-ionic detergent (Lissapol N) and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing. Samples of fabric were run in a bath containing 1.5% BAP, 1.5% DLH oww and between 4 and 10 g/l MgCl<sub>2</sub>. The temperature was set at 50°C, pH 7 and maintained until exhaustion was 60 complete. Fabric samples were then heat cured at 140°C for 15 minutes. 60

5	Example No.	MgCl <sub>2</sub> conc. g/l	Time to Exhaustion (min.)	Area Shrinkage (%)		5
				1 hr wash	3 hr wash	
	44	4	44	1	4	
	45	6	22	0	6	
10	46	8	11	1	3	10
	47	10	7.5	0	5	
	Untreated fabric			70		

- 15 *Examples 48-50* 15
- Example 45 was repeated using 2% BAP (solids oww) and 1% DLH (solids oww) at pH 7, 50°C, maintained until exhaustion complete. Samples were then either:
- (a) removed from the bath at pH 7 and tumble dried,
- 20 (b) cured in the bath by raising the pH to 8 and holding for 10 minutes followed by tumble 20  
drying, or
- (c) cured in the bath by raising the pH to 9 and holding for 10 minutes followed by tumble  
drying.

25	Example No.	Curing conditions	Area Shrinkage (%)		25
			1 hr	3hr	
30	48	Removed at pH 7	1	15	30
	49	Bath to pH 8 for 10 min.	1	1	
	50	Bath to pH 9 for 10 min.	1	1	

- 35 *Examples 51-53* 35
- Samples of fabric cured as in Examples 48 to 50 were then dyed with a chrome dye, Eriochrome Black PV 200%, without drying. The dyebath contained:
- 4% Eriochrome Black PV 200%
- 3% Acetic acid (oww)
- 40 Dye and acid were added to the bath at 30°C and the fabric run for 10 minutes. The 40  
temperature was then raised to the boil over 45 minutes and held for 30 minutes. 1.5% formic  
acid was then added and boiling continued for a further 30 minutes when the bath was cooled  
to 80° and 1.5% potassium dichromate added. The bath was returned to the boil and held for  
45 minutes, followed by cold rinsing and tumble drying. An untreated control was included in 45  
the dyebath. Wash results were:-

50	Example No.	Curing Conditions	Area Shrinkage during dyeing	Area Shrinkage (%)		50
				1 hr	3 hr	
	51	Bath to pH 9 × 10 min.	0	3.0	14.0	
	52	Bath to pH 8 × 10 min.	0	8.6	12	
	53	Removed at pH 7	6.0	70%	—	
55	—	Untreated wool	7.4	72%	—	55

*Examples 54-56*

- Example 45 was repeated on a Shetland fabric. The fabric was knitted to a cover factor of 0.9  
60 from 2/8's Shetland yarn. The fabric was scoured with 1 g/l non-ionic detergent (Lissapol N) 60  
and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing.
- Samples were heated in a bath of liquor ratio 40:1 set at pH 7 and 50°C containing 6 g/l  
MgCl<sub>2</sub> and either 2.5%, 2.0% or 1.5% (solids) oww BAP/DLH at a ratio of 1:1. The  
temperature and pH were maintained until exhaustion was complete. Fabrics were then heat  
65 cured at 140°C for 15 minutes. 65

5	Example No.	% BAP/IMP oww	Time to Exhaustion (min.)	Area Shrinkage (%)		5
				1 hr wash	3 hr wash	
	54	2.5	45	0	0	
	55	2.0	40	1.8	2.3	
10	56	1.5	45	1.4	6.25	10
	Untreated fabric			35	61	

15 *Examples 57-59* 15

Example 54 was repeated using different curing conditions. Exhaustion was complete in 60 minutes. Fabrics were then cured as follows:

- (i) Removed at pH 7 and tumble dried at 100°C for 20 minutes.  
(ii) Bath pH raised to pH 8 and held for 15 minutes, tumble dried at 100°C for 20 minutes.  
20 (iii) Bath pH raised to pH 9 and held for 15 minutes, tumble dried at 100°C for 20 minutes. 20

25	Example No.	Curing conditions	Area Shrinkage (%)		25
			1 hr wash	3 hr wash	
	57	Removed at pH 7	4.5	10.5	
	58	Bath to pH 8 for 15 min.	0.8	2	
30	59	Bath to pH 9 for 15 min.	3	1.9	30

*Example 60*

500 g of a 4/8's hand knitting yarn were scoured in a laboratory hank dyeing machine at a liquor ratio of 30:1 containing 1 g/l nonionic detergent (Lissapol N) and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing. The bath was then set at a liquor ratio of 30:1 at pH 9, 50°C, containing 3.0% (solids) oww BAP/IMP/ANIL DLH at a ratio of 1:1 and 4 g/l MgCl<sub>2</sub>. The pH and temperature were maintained until exhaustion was complete. The yarn was then rinsed and dried at 140°C for 15 minutes. Samples of fabric were then knitted to a cover factor of 0.9 and wash tested in the Cubex machine with the following results:

45		Area Shrinkage (%)		45
		1 hr	3 hr	
	Treated 3% BAP/DLH	6.5	12	
	Untreated	58	—	

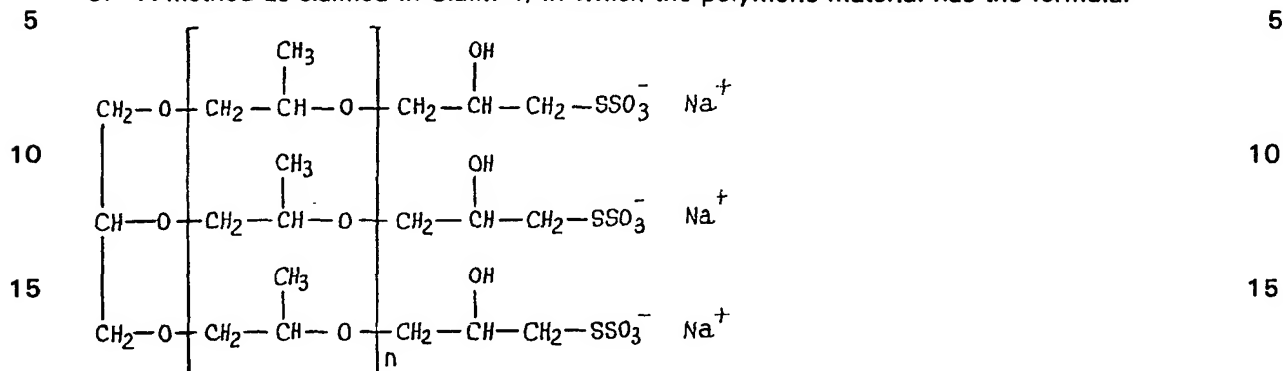
## 50 CLAIMS 50

1. A method of treating textiles which comprises applying to the textile a water-soluble curable polymeric material in an aqueous medium, simultaneously or subsequently applying to the textile a compatible exhaustion agent which reduces the solubility of the polymeric material, allowing the polymeric material to exhaust onto the textile and curing the polymeric material.
- 55 2. A method as claimed in Claim 1, in which the polymeric material is a polymer having ionic charges. 55
3. A method as claimed in Claim 2, in which the polymeric material is a Bunte salt compound or a poly(carbamoylsulphonate).
4. A method as claimed in Claim 2, in which the curable polymeric material has a polymeric chain backbone and at least two thiosulphate groups per molecule.
- 60 5. A method as claimed in Claim 2, in which the polymeric material has been prepared from a polymeric di- or poly-isocyanate by reaction with a bisulphite. 60
6. A method as claimed in Claim 4, in which the polymeric material comprises a polymeric chain backbone and at least two isocyanate groups per molecule.
- 65 7. A method as claimed in Claim 4 or 6, in which the polymeric backbone chain is a 65

polyoxyalkylene chain.

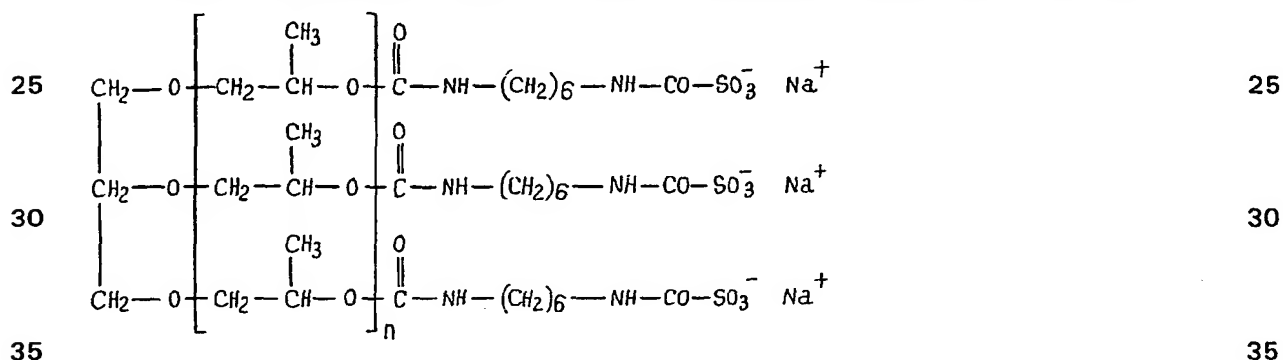
8. A method as claimed in Claim 7, in which the polyoxyalkylene chain is a polyoxypropylene chain.

9. A method as claimed in Claim 4, in which the polymeric material has the formula:



20 where n is about 13.

10. A method as claimed in Claim 5, in which the polymeric material has the formula:



where n is about 13.

11. A method as claimed in any of claims 1 to 10, in which the amount of polymeric material applied is between  $\frac{1}{2}$  and 10% on the weight of fibres.

40 12. A method as claimed in Claim 11, in which the amount of polymeric material applied is in the range of 2 to 4% on the weight of the fibres.

13. A method as claimed in any one of claims 1 to 12, in which the polymeric material is cured by means of an alkali.

45 14. A method as claimed in Claim 13, in which alkali is present in the aqueous medium containing the polymer from the start of the process.

15. A method as claimed in Claims 1 to 4, in which the alkali is pre-mixed with the polymeric material for an ageing period before application to the textile.

16. A method as claimed in Claim 15, in which the ageing period is from 10 to 60 minutes.

50 17. A method as claimed in Claim 13, in which the alkali is applied after exhaustion of the polymer from the aqueous medium.

18. A method as claimed in any one of claims 13 to 17, in which the alkali is ammonium hydroxide or trisodium phosphate.

19. A method as claimed in any one of Claims 13 to 18, in which sufficient alkali is used to ensure a pH value of 8 to 10.

55 20. A method as claimed in any one of claims 1 to 9, in which the exhaustion agent is neutral inorganic salt.

21. A method as claimed in Claim 20, in which the inorganic salt is selected from alkali metal, alkaline earth metal and ammonium salts of strong acids.

60 22. A method as claimed in Claim 21, in which the exhaustion agent is selected from sodium sulphate, sodium iodide, sodium chloride, magnesium sulphate, ammonium sulphate, calcium chloride and zinc sulphate.

23. A method as claimed in Claim 21, in which the exhaustion agent is magnesium chloride.

65 24. A method as claimed in any one of claims 1 to 23, in which the amount of exhaustion agent used is between 1 and 100 g/l of the treatment liquor.

25. A method as claimed in Claim 24, in which the amount of exhaustion agent is between 5 and 10 g/l of the treatment liquor.
26. A method of treating textiles as claimed in Claim 1, using a short liquor, in which;
- (i) the polymeric material and alkali are mixed and allowed to age;
  - 5 (ii) the liquor from (i) is applied to the goods in a washing machine or milling machine; 5
  - (iii) the goods are agitated until a uniform distribution of the liquor is obtained;
  - (iv) a solution of inorganic salt is sprayed onto the goods and agitation continued until it is evenly distributed; and
  - (v) the goods are rinsed, hydroextracted and dried.
- 10 27. A method of treating textiles as claimed in Claim 1, using a long liquor in which; 10
- (i) the polymer and alkali are mixed and added to the bath containing the goods;
  - (ii) the solution of the inorganic salt is added and the temperature raised to 50°C;
  - (iii) after about 30 minutes a further addition of inorganic salt is added; and
  - (iv) after a further 15 to 30 minutes the goods are hydroextracted and dried.
- 15 28. A method as claimed in any one of Claims 1 to 27, wherein the textile material is a 15  
keratinous material.
29. A method as claimed in Claim 28, wherein the textile material is wool.
30. A method as claimed in Claim 28 or 29, wherein the textile material is in the form of knitted piece goods or garments.
- 20 31. A method as claimed in Claim 1, conducted and substantially as described in any of 20  
Examples 1 to 60, herein.
32. Textiles wherein treated by a method as claimed in any of Claims 1 to 31.

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REPLACED BY  
ART 34 AMDT

- 3 -

The advantages include increased dimensional stability of the fabric.

The present invention also seeks to improve the surface  
5 colour definition and/or the handle of the fabric in both industrial textile treatment processes and in small and large scale laundering processes.

According to the present invention, there is provided a  
10 fabric care composition, adapted for use in a laundering process, comprising an anionic polymer which is capable of self cross-linking and/or reacting with cellulosic fibres and further comprising a fabric conditioning agent which acts as a textile compatible exhaustion agent for the  
15 anionic polymer.

Surprisingly, the anionic polymers can impart benefits to fabrics containing cellulosic fibres (such as cotton) in a laundering process. The benefits include increased  
20 dimensional stability and/or improved surface colour definition and/or softer handle. The dimensional stability of a fabric is generally a measure of its resistance to shrinkage. However, the term "dimensional stability", and related terms, used herein covers not only shrinkage of  
25 fabrics but also shape retention, bagginess reduction and additionally, although less preferred, crease/wrinkle resistance in fabrics.



- 5 -

Polymers in which Y is  $-\text{CO}-\text{NH}-(\text{CH}_2)_p-\text{NH}-\text{CO}-$  are commercially available under the Trade Mark SYNTHAPPRET BAP (Bayer).

Polymers in which Y is  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-$  are available under  
5 the Trade Mark NOPCOLAN SHR3 (Henkel).

Conditioning/exhaustion agents which are suitable for use in the compositions of the invention include water soluble or water dispersible compounds comprising one or more cationic  
10 groups. The cationic groups are preferably quaternary ammonium cations.

Preferred materials include HEQ (1,2-bis-[hardened tallowoyloxy]-3-trimethylammonium propane chloride), for  
15 example.

In the present invention, quaternary ammonium cations such as HEQ have the dual function of acting as both exhaustion agents and as fabric conditioning/softening compounds, as  
20 described hereinafter.

Optionally, other cationic species, which do not act as fabric softening compounds, such as other predominantly organic cations and simple metal cations (eg magnesium), for  
25 example, may also be used as additional exhaustion agents in the fabric care compositions of the invention. The compositions of the invention may contain one textile compatible exhaustion agent or a mixture of two or more textile compatible exhaustion agents.

30



- 9 -

wherein  $R_1$ ,  $p$  and  $R_2$  are as defined above.

It is advantageous if the quaternary ammonium material is  
5 biologically biodegradable.

Preferred materials of this class such as 1,2-bis (hardened  
tallowoyloxy) -3-trimethylammonium propane chloride and  
their methods of preparation are, for example, described in  
10 US 4 137 180 (Lever Brothers Co). Preferably these  
materials comprise small amounts of the corresponding  
monoester as described in US 4 137 180, for example, 1-  
hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane  
chloride.

15

Other useful cationic softening agents are alkyl pyridinium  
salts and substituted imidazoline species. Also useful are  
primary, secondary and tertiary amines and the condensation  
products of fatty acids with alkylpolyamines.

20

The compositions may alternatively or additionally contain  
water-soluble cationic fabric softeners, as described in GB  
2 039 556B (Unilever).

25 The compositions may comprise a cationic fabric softening  
compound and an oil, for example as disclosed in EP-A-  
0829531.

The compositions may alternatively or additionally contain  
30 nonionic fabric softening agents such as lanolin and  
derivatives thereof.



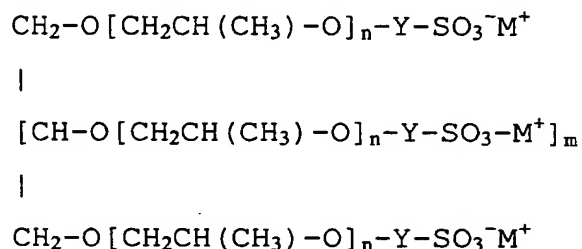
- 19 -

**CLAIMS**

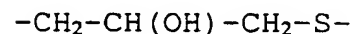
1. Fabric care composition, adapted for use in a  
laundering process, comprising:
- 5 a) an anionic polymer which is capable of self cross-  
linking and/or of reacting with cellulosic fibres and  
further comprising
- b) a fabric conditioning agent which acts as a textile  
compatible exhaustion agent for the anionic polymer.

- 10 2. Composition as claimed in Claim 1, wherein the polymer  
is selected from carbamoyl sulphonate terminated  
poly(ether)urethane resins, bunte salt terminated  
polymers and mixtures thereof.

- 15 3. Composition as claimed in Claim 2, wherein the polymer  
is of the formula (I):



25 wherein: Y is a divalent radical selected from



and  $-\text{CO-NH-}(\text{CH}_2)_p\text{-NH-CO-}$

30

